

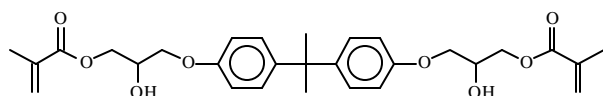
## Synthesis, Characterization and Evaluation of Urethane Derivatives of Bis-GMA

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### Introduction

2,2-bis[p-(2'-hydroxy-3'methacryloxypropoxy)phenyl]propane (Bis-GMA) is currently widely used as a base monomer in polymeric dental materials, e.g. restorative composites, adhesives and prophylactic sealants. This monomer, which also finds use as a commercial vinyl ester matrix monomer for structural composites, is synthesized by reacting glycidyl ester methacrylate with bisphenol A or alternatively, by reacting diglycidyl ether of bisphenol A and methacrylic acid.<sup>1</sup> The structure of the major product of these reactions, which has been given the acronym Bis-GMA, is shown below.



Bis-GMA

Advantages of using Bis-GMA over smaller-sized dental monomers, such as methyl methacrylate, include less shrinkage, higher modulus and reduced toxicity due to its lower volatility and diffusivity into tissues. These desirable properties of Bis-GMA are partially negated by a relatively high viscosity and low vinyl conversion under ambient polymerization conditions. Thus, the use of a less viscous monomer as a diluent comonomer, e.g. triethyleneglycol dimethacrylate (TEGDMA), to achieve a resin of workable viscosity is a common practice. Unfortunately, the addition of smaller-sized diluent comonomers increases polymerization shrinkage and contributes to the development of concomitant stress sites in the polymeric dental materials and its interface with tooth structure, resulting in interfacial gaps and promoting microleakage. Moreover, the hydroxyl groups of Bis-GMA are a major source of the relatively high water absorption of Bis-GMA based polymeric matrices which can have adverse effects on the properties of dental materials.

The high viscosity of Bis-GMA, derived primarily from the hydrogen bonding of the hydroxyl groups, can be reduced by their conversion to other functional groups such as esters.<sup>2</sup> This can lead to derivative monomers that are less viscous and less hydrophilic than Bis-GMA, but that also yield polymers with lower flexural strength and moduli. Another approach to less viscous and more hydrophobic monomers involves removal of pendant hydroxyl groups by substitution of ethylene oxide groups between the bisphenol A core and the methacrylate groups; these monomers also yield polymers with relatively lower flexural strengths and moduli. These and other similar types of derivatives of Bis-GMA,<sup>3,5</sup> however, should be useful as compatible, low shrinking diluent comonomers for Bis-GMA and similar base monomers. In this study, we have reacted Bis-GMA with mono-functional alkyl isocyanates (RNCO) of varying chain length. The resulting urethane group is known to form weaker hydrogen bonds compared to the hydroxyl group but is expected to have higher cohesive energy density than ester or ether linkages. These urethane derivatives of Bis-GMA are expected to have much lower viscosities and water uptake than Bis-GMA and exhibit higher conversion of vinyl groups without excessively increasing polymerization shrinkage of dental resin systems.

### Experimental<sup>##</sup>

Bis-GMA was reacted with stoichiometric amounts of the various alkyl isocyanates in dry dichloromethane under reflux conditions as shown in **Scheme 1**.<sup>6</sup> A catalytic amount of disobutyltin dilaurate was added to the reaction mixture. The reaction was followed by FTIR spectroscopy by monitoring the disappearance of isocyanate peak to yield virtually quantitative amount of product. After solvent removal by rotary evaporator under increasing vacuum, FTIR, proton and carbon NMR were recorded to confirm the structure of product and also the complete removal of dichloromethane. Refractive index was measured using a Bausch & Lomb refractometer at 22.5 °C. The relative standard uncertainty in each point was 0.5 %.

Viscosity was measured with a Rheometric Scientific ARES controlled-strain rheometer, in the steady rate sweep mode. Measurements were made in both clockwise and counter-clockwise directions, and then averaged. In each direction, at each shear rate, shear was applied for 100 s before measuring, then the torque was measured for 30 s. The fixtures used were 25 mm, 0.04 rad cone and plate. All measurements were made at 25 °C. The relative standard uncertainty in each point was 0.5 %.

Camphorquinone (0.6 mol%) and ethyl 4-*N,N*-dimethylaminobenzoate (mole fraction, 2%) were used as the photoinitiator system. For the determination of degree of vinyl conversion, monomer specimens in teflon molds (5 mm diameter and 1.5 mm thickness) were irradiated with visible light (TRIAD 2000, Dentsply) of an intensity of 66  $\mu\text{W}/\text{cm}^2$  for 60 s per side. The degree of vinyl conversion was determined by near infrared spectroscopy.<sup>7</sup> The vinyl double bond of these methacrylate monomers appears at 6165  $\text{cm}^{-1}$  in the near infrared region. For calculating the degree of vinyl conversion this peak area was compared in the monomer and in the photocured polymer. The ratio of area normalized to the thickness of the sample leads to the degree of vinyl conversion. The relative standard uncertainty in each point was 0.7 %. Volumetric shrinkage was measured using a computerized mercury dilatometer which used a Spectrum Curing Visible Light (Caulk/Dentsply). Weighed specimens on glass slides were polymerized for 60 s.

Flexural Strength (FS) was measured in three point bending mode (Instron 5500R) on specimens (27 mm x 2 mm x 2 mm) cured for 60 s per side with the TRIAD 2000 unit. Water uptake was measured by soaking known weights of the vacuum dried photocured monomers (5 mm diameter and 1.5 mm thickness) in distilled water and then recording the weight gain of the polymers with time.

### Results and Discussion

Reaction of stoichiometric amounts of each isocyanate with Bis-GMA yielded urethane derivatives of Bis-GMA in virtually quantitative yield. A number of straight chain alkyl isocyanates (RNCO) with R = ethyl, propyl, butyl, hexyl and octyl groups were employed in this study. An important consideration in the formulation of esthetic dental composites with high conversions and depths of cure is how well the refractive indices of the polymer matrices match those of the reinforcing fillers. Typical radiopaque fillers such as those containing barium, strontium and zirconium have refractive indices of about 1.55. **Table 1** shows the refractive index and the degree of vinyl conversion for the urethane modified Bis-GMAs. The refractive indices obtained are comparable to Bis-GMA but decreases somewhat as the length of the side chain is increased. The refractive indices are expected to be slightly higher for their polymers. The refractive index of TEGDMA, a widely used diluent for Bis-GMA, is 1.460. Hence, its addition to Bis-GMA will not only decrease viscosity but also the refractive index of the resin system. Another widely used dental monomer is the aliphatic diurethane dimethacrylate (UDMA) which has a refractive index of 1.480.

**Table 1. Refractive Index and Degree of Conversion of Urethane Modified Bis-GMAs**

Resin	Refractive Index at 22.5 °C	% Conversion
Bis-GMA	1.549	52.40
Bis-GMA/EtNCO	1.530	83.19
Bis-GMA/PrNCO	1.524	87.97
Bis-GMA/ButNCO	1.518	87.30
Bis-GMA/HexNCO	1.516	91.49
Bis-GMA/OctNCO	1.513	90.68

The degree of vinyl conversion, determined from near infrared spectroscopy, was considerably higher for the urethane modified Bis-GMAs compared with Bis-GMA.

As shown in **Figure 1** the viscosities of urethane modified Bis-GMA monomers were significantly lower compared to that of Bis-GMA. The low viscosity of urethane modified Bis-GMA monomers compared to Bis-GMA is due to the increase in mobility due to the side chains and the weaker hydrogen bonding of the urethane groups compared to the stronger interactions of the hydroxyl groups of Bis-GMA.

The values for fractional volumetric shrinkage for Bis-GMA, Bis-GMA/EtNCO, Bis-GMA/PrNCO, Bis-GMA/ButNCO, Bis-GMA/HexNCO and Bis-GMA/OctNCO are 3.43 % (0.06), 4.20 % (0.01), 4.15 % (0.12), 4.18 % (0.15), 4.20 % (0.01), 4.08 % (0.05) respectively. The values in parenthesis are the average standard deviation of the mean values for n =3. The lower shrinkage value for Bis-GMA reflects its lower conversion compared to the urethane modified Bis-GMA. The polymerization shrinkage of the modified Bis-GMA would be lower than Bis-GMA if compared at constant conversion values.

The water uptake experiment showed that all the modified Bis-GMA polymers were less hydrophilic compared to the Bis-GMA polymer and, as the length of the hydrocarbon side chain was increased, the modified BisGMA polymers became increasingly hydrophobic (Figure 2).

All modified Bis-GMA polymers had lower flexural strengths compared to that of the Bis-GMA polymer (Table 2). The values in parenthesis represent the standard deviation of the mean, n=5.

**Table 2. Flexural Strength (FS) of Urethane Modified Bis-GMA**

Resin	Flexural Strength (Mpa)
Bis-GMA	85.9 (13.2)
Bis-GMA/EtNCO	79.2 (7.2)
Bis-GMA/PrNCO	55.6 (13.9)
Bis-GMA/ButNCO	57.6 (4.5)
Bis-GMA/HexNCO	54.0 (4.9)
Bis-GMA/OctNCO	47.5 (5.6)

Both the length of the hydrocarbon chain, which acts as a flexibilizing substituent, and the weaker hydrogen bonding interactions of the urethane groups contributes to lower mechanical properties for these modified Bis-GMA polymers.

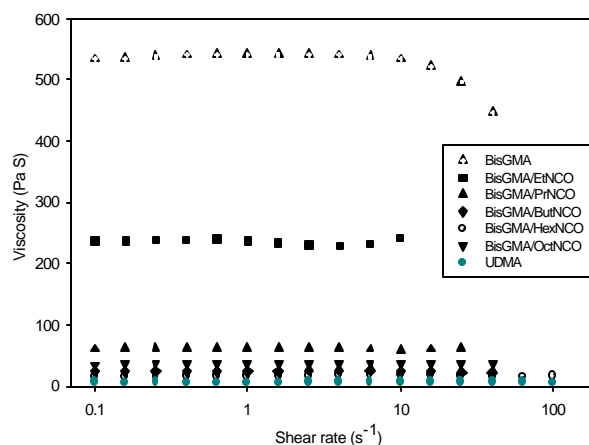
Currently we are investigating the use of these and similar urethane modified Bis-GMA as comonomers with Bis-GMA, UDMA and other base resin systems in an effort to develop polymeric dental composites with improved properties especially those having low polymerization shrinkage and water uptake with high vinyl conversion.

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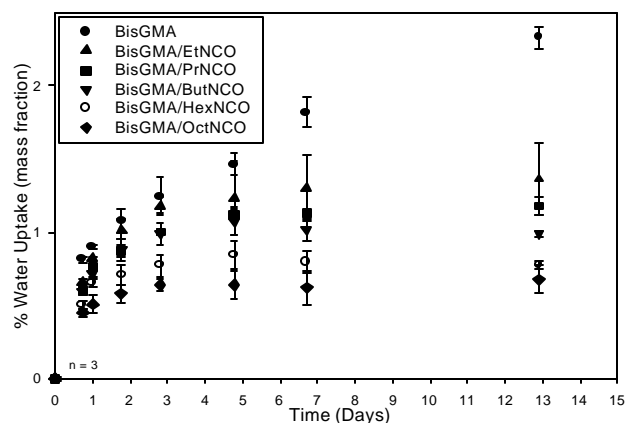
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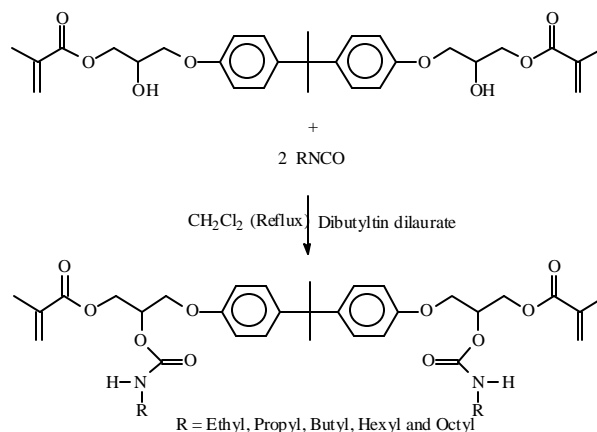
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**Figure 1.** Viscosity as a function of shear rate for urethane modified Bis-GMA at 25 °C.



**Figure 2.** % Water uptake as a function of time for urethane modified Bis-GMA. (Each point represents a mean value of 3 different determinations; relative standard uncertainty is between 2 % – 20 %)



**Scheme 1.** Synthesis of Urethane modified Bis-GMA.